

1 TO WHOM IT MAY CONCERN:

2

3 BE IT KNOWN THAT WE, DAVID W. WARREN, a  
4 citizen of the United States of America, residing in  
5 Van Nuys, in the County of Los Angeles, and MICHAEL B.  
6 DONAHUE, a citizen of the United States of America,  
7 residing in La Verne, in the County of Los Angeles,  
8 both in the State of California, have invented a new  
9 and useful improvement in

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12 **THERMALLY-INTEGRATED LOW TEMPERATURE WATER-GAS SHIFT**

13 **REACTOR APPARATUS AND PROCESS**

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1 BACKGROUND OF THE INVENTION

2  
3 This invention relates to a process and an  
4 apparatus for producing hydrogen for application to  
5 fuel cell electric generators.

6 Catalytic reaction apparatus and processes  
7 for converting hydrocarbon feedstocks to useful  
8 industrial gases, such as hydrogen, is well known in  
9 the art. Proton exchange membrane (PEM) fuel cells  
10 have emerged as a viable option for the production of  
11 disbursed electrical power, typically in the range of  
12 2-50 k W, for use in residential and small commercial  
13 applications. PEM fuel cells generate electricity by  
14 the electrochemical reaction between hydrogen and  
15 oxygen.

16 While oxygen is readily available from  
17 ambient air, hydrogen must be produced from  
18 commercially available fuels, such a natural gas or  
19 propane, using methods such as steam reforming. Steam  
20 reforming is a process that involves a high temperature  
21 catalytic reaction between a hydrocarbon and steam to  
22 form a hydrogen-rich product gas, commonly referred to  
23 as reformat, that contains significant quantities of  
24 carbon monoxide.

1                Since PEM fuel cells have a low tolerance to  
2 carbon monoxide, the concentration of carbon monoxide  
3 in the reformat must be reduced using a catalytic  
4 reaction step known as the water-gas shift reaction.  
5 Following the water-gas shift reaction, the  
6 concentration of carbon monoxide in the reformat is  
7 further reduced to concentrations typically less than  
8 10 ppm using a selective oxidation reaction, also  
9 referred to as preferential oxidation or PROX. The  
10 combination of processes that convert commercial fuels  
11 to a reformat suitable for use in a fuel cell is  
12 commonly referred to as a fuel processor.

13                As an illustration, Table 1 summarizes the  
14 reaction steps of a fuel processor designed to produce  
15 a hydrogen-rich gas stream suitable for use in a PEM  
16 fuel cell.

17  
18                Table 1. PEM fuel processor reaction steps

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20	1. $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + \text{H}_2$	Steam reforming
21	2. $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$	Water-gas shift
22	3. $\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$	Selective oxidation

23

24                In typical industrial practice, the water-gas  
25 shift reaction is conducted in two separate adiabatic  
26 reactors operating at two different temperature

1 regimes. The first reactor, known as the high  
2 temperature shift reactor, operates at inlet  
3 temperatures typically ranging from about 550°F to  
4 650°F. The second reactor, known as the low  
5 temperature shift reactor, operates at an inlet  
6 temperature typically ranging from about 380°F to  
7 450°F. The combination of the two sequential water-gas  
8 shift reactions typically reduces the concentration of  
9 carbon monoxide in the reformat to less than 1.0  
10 volume percent.

11           The use of a low temperature shift reactor is  
12 beneficial because the water-gas shift reaction is  
13 thermodynamically favored at lower temperatures.  
14 However, a high temperature shift reactor is generally  
15 required to limit the amount of heat that is released  
16 in the low temperature shift reactor.

17           Conventional low temperature shift catalysts  
18 comprise a mixture of copper and zinc that are  
19 supported on a ceramic carrier. These catalysts  
20 promote the water-gas shift reaction at lower  
21 temperature, but lose activity if they are exposed to  
22 excessively high temperatures due to sintering of the  
23 active metals. Therefore, it is generally desirable to  
24 limit the maximum temperature of the low temperature  
25 shift catalyst to about 500°F in order to achieve long  
26 catalyst life.

1           The water-gas shift reaction releases  
2   approximately 9837 calories per gram-mole of carbon  
3   monoxide that is consumed. If the water-gas shift  
4   reaction were conducted using a single adiabatic low  
5   temperature shift reactor, the heat release would  
6   result in a temperature increase across the catalyst  
7   bed that would exceed the desirable temperature limit  
8   for conventional low temperature shift reactors.  
9   Furthermore, the high exit temperature from the water-  
10   gas shift reactor would be thermodynamically less  
11   favorable for achieving high conversions of carbon  
12   monoxide.

13           There is need to minimize the number of  
14   reactors and heat exchangers that are needed to achieve  
15   the objective of high conversion of carbon monoxide for  
16   PEM fuel cell applications, in order to reduce the  
17   size, cost and complexity of the fuel processor.  
18   Therefore, it is desirable to conduct the water-gas  
19   shift reaction using a single reactor vessel that is  
20   maintained within acceptable operating temperature  
21   limits by controlling heat removal from the reactor.

22           The steam reforming reaction requires large  
23   quantities of steam for the conversion of hydrocarbon  
24   to reformat. It is desirable to recover the heat  
25   released from the water-gas shift reaction for the  
26   purpose of generating steam in order to improve the

1 thermal efficiency of the fuel processor. The present  
2 invention achieves the objective of temperature control  
3 and heat recovery by integrating a lower temperature  
4 shift reactor within a steam generator that contains  
5 water boiling at a temperature range of about 360°F to  
6 400°F, corresponding to a boiler pressure of about 153  
7 psia to 247 psia.

8           Because the vessel walls of the lower  
9 temperature shift reactor are in heat transfer  
10 communication with boiling water, the heat released  
11 from the water-gas shift reaction is effectively  
12 removed to control the temperature in the catalyst bed  
13 within the desired operating temperature range.  
14 Furthermore, the heat released from the water-gas shift  
15 reaction is beneficially recovered to generate steam  
16 that is used in the process. Finally, the steam  
17 generator provides a convenient source of heat for  
18 heating the catalyst bed during start-up.

19           U.S. Patent 6,086,840 describes a process for  
20 making ammonia that mentions use of an isothermal shift  
21 reactor that includes heat exchange tubes extending  
22 within a vessel packed with catalyst. The heat  
23 exchange tubes contain a boiling fluid to remove heat  
24 from the catalyst bed.

25

Year	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100
1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	

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1 conversion of hydrocarbon feedstock into hydrogen-rich  
2 gases,  
3           b) an outer annulus extending about said  
4 waste-heat steam generator,  
5           c) a catalyst bed located within said outer  
6 region, and through which reformat gases flow,  
7           d) the outer region being in heat transfer  
8 communication with the steam generator to maintain the  
9 catalyst bed within a predetermined temperature range  
10 for operation of a low temperature shift reaction.

11           These and other objects and advantages of the  
12 invention, as well as the details of an illustrative  
13 embodiment, will be more fully understood from the  
14 following specification and drawings, in which:

15  
16                           **DRAWING DESCRIPTION**

17  
18           Fig. 1 is a flow diagram of a process that  
19 incorporates a thermally-integrated low temperature  
20 water-gas shift reactor;

21           Fig. 2 is a schematic showing of apparatus  
22 for testing a thermally-integrated low temperature  
23 water-gas shift apparatus;



1           Fig. 3a is a schematic showing of a  
2 thermally-integrated low temperature water-gas shift  
3 reactor apparatus;

4           Fig. 3b is a section taken on lines 3b-3b of  
5 Fig. 3a; and

6           Fig. 4 is a schematic showing of an alternate  
7 thermally-integrated low temperature water-gas shift  
8 reactor apparatus.

9

## 10                           **DETAILED DESCRIPTION**

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### 12           **PROCESS AND APPARATUS**

13

14           The process and apparatus as shown in Fig. 1  
15 controls the temperature of a low temperature shift  
16 reactor and makes beneficial use of the heat of  
17 reaction to generate steam that is employed to produce  
18 hydrogen-rich gases containing low concentrations of  
19 carbon monoxide from hydrocarbon feedstocks.

20           A reactant mixture at 1 consists of  
21 hydrocarbon feedstock 32 and steam 11. The mixture is  
22 preheated in an exchanger 2 and introduced into a  
23 tubular catalytic reactor 3 that is contained within a  
24 combustion chamber 4. The tubular catalytic reactor  
25 typically contains a supported Ni catalyst and is

1 commonly referred to in the industry as a steam  
2 reformer. Fuel 5 and air 6 are combusted in the  
3 chamber 4 to heat the reactant mixture so as to produce  
4 a hydrogen-rich stream 7 containing carbon monoxide  
5 concentrations typically ranging from 5% to 15%.

6  
7 Combustion products 8 from the combustion  
8 chamber pass through a flue gas heat exchange coil 9  
9 that is contained within a waste heat steam generator  
10 10, wherein the combustion products are cooled and steam  
11 11 is generated. The cooled combustion products 13 are  
12 further cooled by exchanging heat in a feed water  
13 exchanger 14 that produces heated water 15 that is  
14 supplied to the waste heat steam generator 10.

15  
16 The hydrogen-rich stream 7 from the tubular  
17 catalytic reactor 3 is cooled in an exchanger 2 to a  
18 temperature typically in the range of 400°F-550°F  
19 whereupon the cooled steam 18 is introduced into a  
20 fixed-bed catalytic reactor 19 shown as surrounding  
21 steam generator 10, to effect a water gas shift  
22 reaction that converts a portion of the carbon monoxide  
23 to hydrogen and carbon dioxide by reaction with steam.  
24 The catalyst bed reactor typically contains a supported  
25 Cu/Zn catalyst and is commonly known in the industry as  
26 a low temperature shift reactor. The walls 20 of the  
low temperature shift reactor are in thermal  
communication with boiling water contained in the waste



1    EXPERIMENTAL DATA

2

3                Tests were conducted to measure the  
4 conversion of carbon monoxide contained in a simulated  
5 reformat gas stream that was passed over a commercial  
6 Cu/Zn catalyst. The Cu/Zn catalyst was contained  
7 within tubular conduit walls that were in thermal  
8 communication with a boiling water fluid. The  
9 objective of the tests was to quantify the relation  
10 between CO conversion and catalyst gas hourly space  
11 velocity (GHSV) as a function of the temperature of the  
12 boiling water fluid.

13                The experimental test system is shown in Fig.  
14 2. The Cu/Zn catalyst 80 was packed in a  $\frac{3}{4}$  inch tube  
15 81 that was surrounded by a metallic water jacket 82.  
16 Steam 83 generated from the water jacket was sent to a  
17 condenser 84 and the condensed liquid 85 was returned  
18 to the water jacket by natural circulation. An  
19 electrical heater 86 was placed on the outer surface of  
20 the jacket and a temperature controller 87 was used to  
21 control the heat input in order to maintain the water  
22 jacket at the desired temperature. A simulated  
23 reformat gas mixture 88 was heated in a pre-heater 89  
24 to a temperature approximately equal to the boiling  
25 water fluid temperature before the gases entered the  
26 catalyst bed. The product gases 90 at the exit of the

1 catalyst bed were cooled, condensed and sent to a gas  
2 chromatograph for compositional analysis. Table 2  
3 summarizes the results for tests conducted using the  
4 experimental apparatus.

5

6 Table 2. Carbon Monoxide exit concentration as a  
7 function of boiler temperature and catalyst space  
8 velocity

9

10 Simulated Reformate Composition at Inlet to Reactor:

11

12		Wet Gas	Dry Gas
13	<u>Component</u>	<u>Vol. %</u>	<u>Vol. %</u>
14	CO	5.70	10.0
15	CO <sub>2</sub>	8.55	15.0
16	H <sub>2</sub>	39.90	70.0
17	CH <sub>4</sub>	2.85	5.0
18	H <sub>2</sub> O	43.00	0.0
19			
20	Total	100.00	100.0

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	Dry Gas GHSV (hr-1)	Boiler Temperature°F	Carbon Monoxide Exit Concentration (Vol.% dry gas)
1			
2			
3			
4	1930	340	3.67
5	762	340	0.62
6	2950	385	2.84
7	2440	385	2.08
8	1930	385	1.70
9	1425	385	0.90
10	1930	398	1.08
11	1425	398	0.55

12  
 13 In order to maximize hydrogen yield and  
 14 minimize the quantity of carbon monoxide that must be  
 15 converted in the selective oxidizer, it is generally  
 16 desirable to achieve less than 1.0 vol.% CO in the dry  
 17 gas at the exit of the shift reactor. It is desirable  
 18 to operate at the maximum space velocity in order to  
 19 minimize the size of the catalyst bed.

20 The results show that when the boiler is  
 21 maintained at temperatures above about 385°F, the CO  
 22 concentration is less than about 1.0 vol.% (dry gas)  
 23 for space velocities less than or equal to about  
 24 1500hr-1. Higher space velocities can be achieved for  
 25 even higher boiler temperatures, however this  
 26 necessitates operation at pressures above 250 psig,

1 which may not be desirable for many PEM fuel cell  
2 applications.

3           The results indicate that there is an optimum  
4 temperature range of operation for the boiler that  
5 achieves the objects of minimum catalyst volume,  
6 moderate boiler pressure and low CO concentration at  
7 the shift reactor exit. This optimum temperature range  
8 is approximately 385°F to 400°F.

9  
10       THERMALLY-INTEGRATED LOW TEMPERATURE WATER-GAS SHIFT  
11                           REACTOR APPARATUS

12  
13           Apparatus shown in Figs. 3a and 3b controls  
14 the temperature of a low temperature shift reactor and  
15 makes beneficial use of the heat of reaction to  
16 generate steam.

17           In the preferred embodiment, the apparatus  
18 comprises an annular catalyst zone 50 within vessel 50a  
19 that is concentrically disposed around an inner steam  
20 generator zone 51 within vessel 51a. The catalyst zone  
21 contains a lower temperature shift catalyst, typically  
22 comprising a catalytically active mixture of copper and  
23 zinc metals, that promote the water-gas shift reaction  
24 at temperatures typically in the range of 370°F to  
25 500°F. The catalyst zone is defined by the annular  
26 space between an outer wall 52 and an inner wall 53.

1 The steam generator zone is defined in the space inside  
2 of the inner wall, a top wall 65, and a tube sheet 66.

3 Reformate containing carbon monoxide enters  
4 an inlet conduit 54 that is in communication with the  
5 annular catalyst zone. The reformate passes through  
6 the catalyst zone, releasing heat due to the exothermic  
7 nature of the water-gas shift reaction. The reformate  
8 exits from the catalyst zone through an exit conduit  
9 55.

10 The inner wall 53 is in thermal contact with  
11 the reformate gases flowing through the catalyst zone  
12 and boiling water 56 contained in the steam generator  
13 zone, the catalyst zone shown as surrounding the steam  
14 generation zone. This results in a transfer of heat  
15 from the catalyst zone to the steam generator zone in  
16 order to maintain the catalyst zone within a defined  
17 temperature range that is optimum for conducting the  
18 low temperature shift reaction.

19 The steam generator zone contains a heat  
20 transfer conduit 57, or a multitude of heat transfer  
21 conduits, that is immersed within the boiling water.  
22 The heat transfer conduit conveys hot combustion  
23 products, such as from the combustion section of a  
24 steam reformer, to transfer heat to the boiling water  
25 for the purpose of generating steam. The hot  
26 combustion products enter an inlet plenum 58 through an



1 inlet conduit 59. The inlet plenum is in communication  
2 with the inlet portion 60 of the heat transfer conduit.  
3 The hot combustion products exit the heat transfer  
4 conduit to an exit plenum 61 that is connected to an  
5 exit conduit 62. Steam that is generated from the heat  
6 transferred to the steam generator zone through the  
7 inner wall 53 and the heat transfer conduit 57 exits  
8 the steam generator zone through an exit conduit 68.  
9 Water is fed to the steam generator zone through an  
10 inlet conduit 69 to maintain the boiling water at a  
11 desired level that is sufficient to efficiently remove  
12 heat from the inner wall and the heat transfer conduit.

13           The annular catalyst zone 50 may include  
14 means to enhance heat transfer between the catalyst bed  
15 and the inner wall 53 such as the use of longitudinal  
16 fins 70 that are attached to the inner wall and extend  
17 a distance into the annular catalyst space. Other heat  
18 transfer enhancements such as metal packing within the  
19 annular catalyst zone, or active catalyst that are  
20 incorporated into highly thermally conductive  
21 monoliths, may be beneficially used in the invention.

## 22

## 23 EXAMPLE

24           A pipe wall having an outside diameter of 5.5  
25 inches defines a waste heat steam generator zone. The  
26 pipe wall is in thermal communication with an annular

1 catalyst zone that is concentrically disposed around  
2 the waste heat steam generator zone. The space between  
3 the 5.5 inch diameter pipe and an outer wall having an  
4 8 inch inside diameter define the annular catalyst  
5 zone. The annular catalyst zone is packed with 4.8 mm  
6 x 2.8 mm low temperature shift catalyst containing  
7 principally a mixture of Cu and Zn supported on a  
8 ceramic carrier. The packed height of the annular  
9 catalyst zone is approximately 12 inches and  
10 corresponds to the approximate height of the water  
11 contained within the waste heat steam generator zone.  
12 The total catalyst volume is approximately 0.184 cubic  
13 feet.

14 The waste heat steam generator zone also  
15 contains heat transfer conduits that are immersed  
16 within the boiling water. The heat transfer conduits  
17 consist of 5/8 inch diameter tubes that are formed in a  
18 u-tube arrangement having inlet means and exit means  
19 that are attached to a single tube sheet. Hot  
20 combustion products from a steam reformer are directed  
21 to the inlet means of the heat transfer tubes. Cooled  
22 combustion products are exhausted from the exit means  
23 of the heat transfer tubes.

24 The waste heat steam generator zone is  
25 operated at a controlled pressure using a back-pressure  
26 regulator that is located on the steam exit conduit.

1 The back-pressure regulator is set at a pressure of 220  
2 psia corresponding to a saturated water temperature of  
3 390°F.

4 Reformat from a tubular catalytic reactor is  
5 cooled to approximately 510°F and is introduced into  
6 the top of the annular catalyst zone. The reformat  
7 exits the bottom of the annular catalyst zone at a  
8 temperature of approximately 430°F. The composition  
9 and flow rate of the reformat at the inlet and exit of  
10 the annular catalyst zone is shown in Table 3.

11  
12 Table 3. Gas composition from thermally-integrated low  
13 temperature water-gas shift reactor

14	15	Gas Composition (Volume %)	
		16 <u>Reformat Inlet</u>	16 <u>Reformat Exit</u>
17	Component		
18	CH <sub>4</sub>	2.1	2.1
19	CO	8.1	0.8
20	CO <sub>2</sub>	7.5	14.7
21	H <sub>2</sub>	52.6	59.8
22	H <sub>2</sub> O	29.7	22.5
23	Total	100.00	100.0
24			
25	Total Flow, SCFH	280	280
26	Temperature, °F	510	430
27	Pressure, psia	16.7	16.7

1       ALTERNATIVE EMBODIMENT OF THERMALLY-INTEGRATED LOW  
2       TEMPERATURE WATER-GAS SHIFT REACTOR APPARATUS  
3

4               Fig. 4 depicts an alternative embodiment of  
5 the thermally-integrated low temperature water-gas  
6 shift reactor apparatus. A helical coil 75 is welded  
7 to the surfaces of the inner wall 53 and outer wall 52  
8 that define the annular catalyst space. The catalyst  
9 is packed within the volumes defined by the helical  
10 coil and the inner and outer walls. The gases entering  
11 the inlet conduit 54 are directed in a helical manner  
12 around the annular space by virtue of the confining  
13 helical coil. This increases the velocity of the gases  
14 within the catalyst bed for a given space velocity in  
15 order to enhance the rate of heat transfer to and from  
16 the bed. The helical coil also serves as an extended  
17 heat transfer surface to enhance the rate of heat  
18 transfer to and from the inner wall of the annular  
19 space. Elements the same as those of Fig. 3a bear the  
20 same identifying numbers.